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Optical Spectroscopy of Strongly Correlated (MOTT-HUBBARD, Heavy-Fermion, Unconventional Superconductor) Materials Tuned Pressure

Alex Goncharov, V. V. Struzhkin

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PROJECT DESCRIPTION

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Optical Spectroscopy at the Insulator-Metal Crossover Induced by High Pressure

PI: Viktor Struzhkin, Geophysical Laboratory, Carnegie Institution of Washington
Co PI: Alexander Goncharov, LLNL, University of California

Summary:

Funding is requested for systematic experimental studies of pressure-induced changes of electronic, magnetic and structural properties of materials with strong electronic correlations (Mott-Hubbard systems, Kondo insulators, unconventional superconductors) at the Insulator-Metal crossover by optical spectroscopy techniques. Pressure is very important variable allowing to tune critical properties of strongly correlated materials in a controllable and reproducible experimental environment through the I-M transition from low to high temperature conditions. This project benefits from numerous inventions in diamond anvil techniques and optical spectroscopy methods developed over last few years. These include progress in Raman and synchrotron infrared instrumentation permitting studies to higher pressures in unattainable previously energy and wide temperature ranges. Recent theoretical predictions regarding the universal features of the Raman response at the I-M crossover will be tested. This includes the predicted isosbestic point in the in the temperature-dependent Raman response at the insulating side of the transition, and the depletion of low-energy response at low temperature. The experiments will focus on pressure effects on coupled lattice, magnetic and electronic degrees of freedom in strongly correlated materials in the regime close to the insulator-metal transition. At the I-M crossover the materials can not be described as Fermi-liquids (on the metal side), or as conventional insulators (on the insulator side), thus the proposed experiments will provide fundamental information on quasiparticle responses in charge and spin channels. Collapse of magnetic moments under pressure will be studied in great detail by tracing the magnetic excitations in some transition metals and their oxides. High-temperature superconductors (HTS) and other prototype materials (V_2O_3, FeSi, and similar classical insulators) will be examined under pressure by Raman spectroscopy in a wide pressure-temperature range on samples with different doping. This will be done to probe various elementary excitations at the I-M crossover: electronic excitations, including pseudogap and superconducting gap excitations, orbital excitations (similar to excitations in $LaMnO_3$), magnetic excitations and their coupling to phonons. The obtained experimental information will provide a broader impact on theoretical models and new concepts at the frontier of current research of strongly correlated materials. A synchrotron IR technique will be used to study optical properties in far-IR and mid-IR spectral ranges and to identify the free electron component and unconventional excitations. Recently developed high-throughput versatile Raman instrumentation that uses extensively holographic optics will be employed. These studies will use synthetic ultra pure diamonds, which have very low fluorescence. We will also develop a new kind of Raman instrumentation based on volume holographic gratings, and further improve our synchrotron IR facility at the NSLS. One postdoctoral associates will be trained in advanced high-pressure optical techniques. The project will make new features of the Raman facility in Washington, DC available for use by external researchers and students under NSF-supported programs (CDAC consortium, COMPRES initiative). This would provide necessary training and stimulate human resources development.

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Introduction.

During the past years, the Co-PI's have been responsible for the development and operation of optical techniques (Raman, IR, fluorescence, absorption and reflectance spectroscopy at ultrahigh pressures and high and low temperatures) which have proven to be extremely powerful for studying low-Z, molecular solids including hydrogen, ice, etc. (see results below). Meanwhile, it has become increasingly clear that optical spectroscopy has an equally extraordinary potential for studying metals and superconductors at ultrahigh pressures, thus the result will have a major impact on material research. However, because of the extreme difference in optical properties of opaque metals and transparent insulating molecular solids, successful accomplishment of the present project will require substantial effort in improving the present equipment and developing new techniques, and funds for this are requested here.

Below we provide a short description of the work done and techniques developed during the last years. We also propose to explore new frontiers in compressed materials close to the insulator-metal boundaries, spin-crossover, and other quantum critical points.

Results From Prior NSF Support

<u>Quantum Effects and the Transition to Non-Molecular Ice.</u> During the first year of the grant, we identified the long-sought, non-molecular or symmetric hydrogen bond state by synchrotron IR spectroscopy techniques (Goncharov, Struzhkin et al. 1996) *(Struzhkin, Goncharov et al. 1997)*. The x-ray measurements indicate that the oxygen sublattice remains close to body-centered cubic (Somayazulu, Goncharov et al. 2000) to at least 210 GPa, with major changes in IR at 60-70 GPa identified as the onset of the transition (Goncharov, Struzhkin et al. 1996). Recent ab initio calculations (Lee, Vanderbilt et al. 1992; Lee, Vanderbilt et al. 1993; Benoit, Marx et al. 1998)are in agreement with the measurements, including calculation of the IR spectrum (Bernasconi, Silvestrelli et al. 1998). Recent Raman measurements carried out with ultrapure synthetic diamonds show the single, strong Raman mode expected for the transition to the Cu_2O structure with classical, symmetric hydrogen bonds (Goncharov, Struzhkin et al. 1999). The transition pressure is constrained to 75±3 GPa on the basis of analysis of the pressure dependence of the low-frequency Raman modes and recently performed far-infrared absorption measurements of the translational mode of ice VII (Goncharov, Struzhkin et al. 2000). Similar conclusions were reached on the basis of a lower pressure IR absorption study (Aoki, Yamawaki et al. 1996). We documented complexities in the vibrational spectra of ice at 20-30 GPa arising from a cascading sequence of Fermi resonances that occur as the soft mode approaches the symmetrization transition (Struzhkin, Goncharov et al. 1997); *(Goncharov, Struzhkin et al. 1999)*. Finally, a new low-pressure phase of ice was found; Raman measurements and optical observations show it has a peculiar morphology and unusual states of order-disorder (Chou, Blank et al. 1998).

<u>Molecular Hydrogen at Ultra-High Pressures</u>. Substantial advances have been made in the study of the phase diagram, nature of the ordered phases, and ortho-para conversion under pressure. The existence of a phase II (or broken symmetry phase) and III (or phase A) has been established in pioneering studies of a Harvard group and Geophysical Lab (Silvera and Wijngaarden 1981; Hemley and Mao 1988; Lorenzana, Silvera et al. 1989; Lorenzana, Silvera et al. 1990). Using Raman spectroscopy at ultrahigh pressures as a tool, PI and co-workers studied the phase diagram of solid D_2 in detail. As a result the triple point between phases I, II, and III has been

established (Goncharov, Mazin et al. 1995). Evidences for other invariant points are found, including one at 182 GPa and 235 K where discontinuity in the vibron frequency through the I-III transition disappears. In ortho-para mixtures of deuterium, phase II behaves as a quantum crystal with molecules orientationally ordered in a possible complex superstructure (Goncharov, Mazin et al. 1996). Hydrogen shows similar to deuterium topography of the phase diagram (Mazin, Hemley et al. 1997). Based on optical study H_2 and D_2 we proposed a united view of orientational ordering in hydrogens, which implies different types of ordering in phases II and III (Mazin, Hemley et al. 1997). The ordering objects in phase II are the angular momenta of rotating molecules, while in phase III the molecules are strongly interacting and undergo an orientational ordering as physical objects, with order parameter behavior close to that of Maier-Saupe transition (Manzhelii and Freiman 1997). The use of ultrapure synthetic single-crystal diamond as anvils allowed new infrared and Raman excitations to be observed in pure para-samples of phase I, II, and III (Goncharov, Hemley et al. 1998). Low-frequency excitations in phase I of pure para hydrogen under pressure have been analyzed theoretically (Goncharov, Strzhemechny et al. 2001). The new vibrational excitations provide important constraints on the crystal structures of phases II and III. Measurements of high quality Raman and infrared spectra have been recently extended to higher pressures (Hemley, Goncharov et al. 1999) *(Goncharov, Struzhkin et al. 1999) (Goncharov, Gregoryanz et al. 2001)* and showed the persistence of the phase III to at least 285 GPa. The earlier discovery of the remarkable enhancement of the infrared response of the vibron (intramolecular stretching mode) in phase III (Hanfland, Hemley et al. 1993) (Cui, Chen et al. 1995) has been the subject of continued study by our group and by a number of theory groups around the world (e.g., (Tse and Klug 1995) (Edwards and Ashcroft 1997) (Kohanoff, Scandolo et al. 1997; Souza and Martin 1998; Kohanoff, Scandolo et al. 1999) (Johnson and Ashcroft 1998) (Soos, Eggert et al. 1994) (Nagao and Nagara 1998) (Kitamura, Tsuneyuki et al. 2000) (Hemley and Ashcroft 1998). Synchrotron infrared techniques indicate no evidence for band-gap closure at the onset of the transition to phase III, and provide new upper bounds to be placed on the optical conductivity at higher pressures within the phase. Measurements for D_2, for example, show transparency down to photon energies of 0.15 eV and pressures to 200 GPa (at 77 K) (Hemley, Mao et al. 1996), in general agreement with the results of other studies at different wavelength ranges and *P-T* conditions (Chen, Sterer et al. 1996) (Eggert, Moshary et al. 1991) (Nayarana, Luo et al. 1998) and theoretical calculations (Johnson and Ashcroft 1998) (Barbee, Cohen et al. 1989) (Chacham and Louie 1991).

Non-Molecular Nitrogen Optical measurements (Goncharov, Gregoryanz et al. 2000)gave the first unambiguous evidence of the transformation to the theoretically predicted (McMahan and LeSar 1985) (Martin and Needs 1986) (Mailhiot, Yang et al. 1992)nonmolecular semiconducting phase of nitrogen.

Synchrotron Spectroscopy Techniques. A custom IR microscope with long-working distance Cassegrain objectives was designed and build at U2B synchrotron IR beamline at the NSLS. It allows concomitant transmission and reflectivity measurements in a wide pressure (to 300 GPa) and low-temperature (L-He) studies (Goncharov, Struzhkin et al. 1996) *(Lu, Goncharov et al. 1999)*. Our successful synchrotron IR facility at the NSLS (beam line U2B) was upgraded to provide wider spectral range and improved performance in both IR and optical (e.g., Raman) measurements (Goncharov and Struzhkin 2000).

Other Spectroscopic Methods. Micro-Raman technique was improved with the use of new CCD detectors and holographic optics (Goncharov and Struzhkin 2000). The use of ultrapure synthetic single-crystal diamond has extended high-sensitivity optical measurements into the multimegabar range (Goncharov, Hemley et al. 1998). A new technique was developed for measuring ruby fluorescence above 250 GPa using a tunable Ti-sapphire laser and holographic filters (Goncharov, Hemley et al. 1998), which complements time-resolved methods (Chen and Silvera 1996).

Human Resource Development

The Geophysical Laboratory is dedicated to the training of pre-doctoral students and post-doctoral fellows in the physical sciences. The following post-doctoral fellows, visiting scientists, research associates and students have received training under PI's and Co-PI's supervision or worked with Co-PI's on the project at the infrared synchrotron beamline and Raman/fluorescence systems: Ming Li (SUNY at Buffalo), Ren Lu (Bayerishes Geoinstitut), J. Badro (Lyon, now at University of Paris), E. Gregoryanz (Memorial U. of Newfoundland), S. Gramsch (Augustana College), J. Xu, J. Z. Hu, J. F. Shu, Eran Karmon (now at UC Berkeley), Jon Eggert (now at LLNL), I-Ming Chou and Robert C. Burruss, U.S. Geological Survey; Sean Shieh (now at Princeton University); Achintya Maddury, Thomas Jefferson high school; Zhenxian Liu, Anurag Sharma, Oliver Tschauner, Holger Hellwig, Yanzhang Ma, Jang Song, Monica Koch-Müller, Sebastien Merkel (Ecole Normale Superieure, Lyon). Senior research associates who worked on projects related to this grant include M. Eremets, M. Somayazulu (also at HPCAT, Chicago).

Proposed research

A. Role of high pressure

The study of the effect of pressure on materials is fundamental to a range of problems in physics (see, e.g. (Hemley and Ashcroft 1998)). With the increasing of pressure, the distances between atoms normally decrease, which leads to the increase of interparticle interactions. Thus, by changing the pressure, one can tune the physical properties of materials, thereby studying phenomena in detail, which includes the change of vibrational, electronic and magnetic properties. The gradual changes of interatomic distances and interaction in some cases yield to radical changes (e.g. phase transitions) of the physical and chemical properties. Many of them are unique in a sense that they can be observed under high pressure only.

The behavior of materials under pressure can now be studied to pressures above 300 GPa (or 3 megabars). This can provide manifold decrease of volume, in many cases giving enough room to see basic changes in bonding character, magnetic or electronic structure or chemical composition. Such experiments are crucial for developing a comprehensive understanding of the most important properties of the matter. They become possible with the development of ultrahigh-pressure diamond-anvil cell techniques. In particular, high-pressure spectroscopy provides crucial and often unique information on bonding properties and physical excitations of metals, semiconductors and superconductors (Hemley and Porter 1988) (Gillet, Hemley et al. 1998).

Ultrahigh-pressure research, by nature, imposes substantial requirements on experimental technique. Very sensitive and versatile equipment is required to work with an extremely small amount of the sample (picoliter volume) brought to megabar pressures. The optical properties of diamond windows next to the high-pressure chamber change dramatically under ultrahigh pressures, thus obliging to modify the technique to these conditions. Thus, the quality of information obtained critically depends on the development of new techniques and improvement of the existing ones.

However, not only ultrahigh-pressure research is important in condensed matter physics. Many important materials have the pressure range of the order of few GPa for complete transformation of their properties. Diamond anvil cell is a versatile tool in this lower pressure range, allowing precise Raman or IR measurements under nearly hydrostatic conditions in the wide temperature range (Goncharov and Struzhkin 2003).

B. Importance of high-pressure optical measurements

Research of behavior of materials at high pressures has been experiencing a great number of advances over last few years (see e.g., (Hemley and Ashcroft 1998) (Hemley and Mao 1996)). As a result of these developments, a broad range of studies of physical properties of solids can be conducted in situ at high pressures to 300 GPa. The (noninclusive) list of developments includes:

-Raman scattering of metals and other low-scattering materials under ultrahigh pressures becomes a routine and has been extended to megabar pressures (Olijnyk 1992) (Merkel, Goncharov et al. 2000) (Liu and Vohra 1994).

-(synchrotron) IR absorption and reflectivity. Routinely extended to far-IR (including magnetospectroscopy (Chen and Weinstein 1996)) and to megabar pressures in mid-IR (Chen, Sterer et al. 1996) (Goncharov, Struzhkin et al. 1999) (Song, Yamawaki et al. 1996) (Goncharov, Struzhkin et al. 1996).

-pressure measurements by ruby fluorescence technique using direct pumping scheme (Chen and Silvera 1996) (Goncharov, Struzhkin et al. 1999) and time-resolved techniques (Eggert, Moshary et al. 1990).

-magnetic susceptibility and electrical conductivity (Struzhkin, Hemley et al. 1997; Struzhkin, Timofeev et al. 1997) (Eremets, Struzhkin et al. 2001)

-x-ray single-crystal and side diffraction (Vohra, Vijayakumar et al. 1984) (Loubeyre, LeToullec et al. 1996) (Struzhkin, Hemley et al. 1997) (Mao, Shu et al. 1998)

-x-ray spectroscopy (Mao, Struzhkin et al. 1997)

-x-ray inelastic scattering (Mao, Xu et al. 2000) (Fiquet, Badro et al. 2001)

Optical techniques still remain among the most informative. They are complementary to other techniques and can be indispensable (e.g., for low-Z materials). This has been shown in a course of accomplishment of our previous research programs (see introduction section). Our preliminary measurements (see below) and literature data lead us to believe that they will be extremely useful for the research proposed. With the techniques available, we are now in the position to attack problems, which had previously been considered as extremely complex, if impossible to solve.

In the course of the proposed project the experience acquired and techniques developed will be applied for more complicated experimental investigations of metals and insulator-metal transitions. In particular, Raman spectra of very weak scatterers will be obtained and optical properties of materials will be studied in a wide spectral range (including far-IR) at megabar pressures. Although some of the techniques were used like in the previous grants, the proposed project is fully independent and covers completely different scope of physical tasks and materials. Moreover, we will further develop our optical techniques for the research proposed.

PROJECT DESCRIPTION

C. Work statement and proposed experiments

We propose to apply the strength of our developed optical methods (Raman and synchrotron IR spectroscopies) for systematic studies of materials close to insulator-metal boundary by tuning their properties under pressure. We will study the effect of pressure and temperature on electronic, vibrational and magnetic excitations in transition metal compounds, to establish crossovers between insulating and metallic states, between magnetically ordered, locally ordered and nonmagnetic states.

We will develop a new generation of Raman spectrometers that use volume holographic gratings extensively. We will also set up a system for measuring of optical properties at ultrahigh pressures in a wide spectral range (from UV to near IR).

The proposed research will answer the following questions**:**

1. Is there a universal electronic scattering across the insulator-metal transition (Freericks and Devereaux 2001) ?
2. How spin crossover transition relates to insulator-metal transition in 3d-metal oxides (Badro, Fiquet et al. 2002) and what are the Raman signatures of the spin-crossover transition?
3. What Raman signatures are relevant to quantum critical point regime?
4. What is the interplay/coupling between electronic, magnetic excitations and phonons near critical points in the phase diagram (Goncharov and Struzhkin 2003)?

These major questions will be addressed in few systems which are already studied by a number of other techniques. We will outline the detailed milestones for the proposed research after brief discussion of the relevance of the Raman technique in addressing all these questions.

Why transition metals?

The role d-electrons play in determining lattice dynamics, electronic and magnetic properties has been of considerable interest in several past decades (Wakabayashi, Scherm et al. 1982) (Lockwood 1982) (Klein 1982). Recent activity is related to a tremendous amount of new phenomena (e.g. high temperature superconductors, colossal magnetoresistance compounds, ferromagnetic superconductors, to name a few examples) discovered in transition metals and their compounds.

We propose to study transition metal containing materials to extend our knowledge about their unique properties (e.g., magnetism, high-temperature superconductivity, etc.) close to insulator-metal transitions, spin-crossover transitions, near quantum critical point (QCP) conditions (Sachdev 2003) by tuning materials by pressure through appropriate regimes. Our strategy will be to focus on representative materials, such as transition metal oxides, prototype high-temperature superconductors, other materials with strong electronic correlations and use a variety of new optical (and other if needed) techniques now available to explore systematically the pressure effects. The properties of different transition metal compounds seem to be unique for some particular compound or composition. Application of pressure allows to tune their properties through the crossovers between different physical states on the *same sample*. Many of the materials have been already studied at ambient pressure and/or with other techniques under pressure, and theoretical calculations are also available. Application of pressure will add new dimension to the study and allow to test existing theories.

A more detailed description of the proposed research is presented below.

Electronic Raman scattering in transition metal oxides

a) Classical systems

The electronic features in Raman spectra of HTSC oxides have been extensively studied by Raman technique at ambient pressure (Reznik, Klein et al. 1992; Blumberg, Kang et al. 1997) (Hackl 1998). Several studies have addressed electronic continuum in cuprates at high pressure conditions (Goncharov and Struzhkin 2003) (Kendziora, Pelloquin et al. 2000). Raman studies of classical systems at ambient pressure are also available, see e. g. "Kondo insulator" FeSi (Nyhus, Cooper et al. 1995). However, there are no systematic studies of Raman scattering at the insulator-metal boundary in compressed materials. We propose to address the effect of compression of the lattice on the Raman signatures of the classical correlated electronic materials V_2O_3 (Carter, Rosenbaum et al. 1991), FeSi (Nyhus, Cooper et al. 1995). This will allow to test recent theoretical predictions regarding the spectral features at the insulator side of the transition (Freericks and Devereaux 2001), and will provide also a wealth of experimental information about Raman scattering at the insulator-metal crossover.

Vanadium sesquioxide V_2O_3 has served as the prototype for both the Mott-Hubbard model of the metal-insulator transition and the Brinkman-Rice picture of the correlated metal. Pure V_2O_3 undergoes a first-order metal-insulator transition at a temperature $T_{MI} \sim 150$ K with drastic changes in the electrical resistivity and antiferomagnetic ordering of the vanadium spins, and a structural transition. The application of the hydrostatic pressure, the adjustment of the oxygen stoichiometry, and alloying with Ti_2O_3 or Cr serve to depress T_{MI}, and can stabilize the metallic phase at all temperatures. This variation of the T_{MI} with internal (chemical) and/or external pressure gives rise to a generalized phase diagram for V_2O_3 which has provided the framework for some of the original studies of highly correlated insulators and metals. The most recent findings are summarized in a paper by Limelette (Limelette, Georges et al. 2003). Our strategy is to use pressure variable for bringing sample through the MI transition around 2 GPa and carefully monitor A_{1g} and B_{1g} Raman response as a function of pressure and temperature. We will use doped samples to bring the transition point below 2 GPa to minimize the depolarization properties of diamond anvils (Kendziora, Pelloquin et al. 2000). The obtained spectra will be compared to existing theoretical models (Freericks and Devereaux 2001).

Interest in iron monosilicide FeSi dates back to the end of 1930s when Foex (Foex 1938) had discovered that the magnetic susceptibilitybof this compound increased with temperature above 200 K. A theoretical model of the unconventional magnetic behavior of FeSi has been proposed in the framework of the general self-consistent renormalization theory of spin fluctuations (Moriya 1985). According to another explanation (Aepply and Fisk 1992), similar to Kondo insulators, FeSi behaves like a local moment system at high temperatures, however, at low temperatures small energy gaps are revealed in the charge (resistivity) and spin (susceptibility) responses. Raman spectra at ambient pressure were interpreted by Nyhus (Nyhus, Cooper et al. 1995) as having an energy gap of the order of 1000 cm^{-1}. Strong coupling and phonon self-energy renormalization effects were found at low temperatures in this Raman study (Nyhus, Cooper et al. 1995). Pressure effect on Raman or IR response in FeSi was never addressed experimentally. We expect that pressure may change significantly the magnetic properties of FeSi and have dramatic effect on both electronic Raman scattering and phonon coupling to electronic subsystem. We propose systematic studies of the pressure effect on Raman and IR response of FeSi from room temperature to low (3K) temperatures, which will allow us to characterize the energy gap feature and electron-phonon coupling in this intriguing material. This study will be supported by electric resistivity and magnetic susceptibility measurements (funded by other sources).

b) High-temperature superconductors

High-temperature superconductivity (HTSC) still remains one of the hottest topics in condensed matter physics. Despite substantial efforts, the nature of the superconducting coherent state is still controversial.

The phase diagram of doped cuprate HTSC (Batlogg and Emery 1996) is intimately connected to the presence of strong electron-electron correlation effects. Underdoped cuprates (parent material) are insulators with anti-ferromagnetic ordering of S=1/2 spins localized at Cu atoms in CuO_2 planes below the Néel temperature T_N. Once the CuO_2 layers are doped, T_N rapidly decreases until metal-insulator transition is reached. In the metal state, the T_C increases with doping until it reaches a maximum at the optimum doping and then decreases, as the system becomes “normal” metal.

In conventional studies the doping level is usually modified by changing the chemical composition (e.g. by changing oxygen content) and thus physically *different samples* with different doping levels are used. Changing pressure instead of chemical doping presents a “clear” way of tuning the properties of the system without changing its chemical composition, since continuous transfer of electrons from the CuO_2 planes normally takes place under pressure. On the other hand, measurements under pressure impose substantial difficulties, making this method not very common.

Raman scattering is a very informative technique for probing phonons, electronic and magnetic excitation, as well as corresponding energy gaps (see, e.g. (Blumberg, Kang et al. 1997)). Raman investigations of HTSC materials under high pressure have been mainly devoted to the behavior of phonons (Payne, Guha et al. 1999) (Osada, Kakihana et al. 1999) (Goncharov, Muinov et al. 1991) (Gasparov, Misochko et al. 1990) (Syassen, Hanfland et al. 1988) and two-magnon features (Aronson, Dierker et al. 1991) (Struzhkin, Goncharov et al. 2000) (Eremets, Lomsadze et al. 1991) since study of much broader and weaker electronic scattering and gap excitations is very complicated due of the diamond fluorescence background. The Stuttgart group, at the time when the PI was there, has been able to tune by pressure in a continuous manner the coupling between the B_{1g} phonon and gap excitation, and, moreover, to observe gap excitations themselves (Goncharov, Struzhkin et al. 1993). In collaboration with Chris Kendzora (NRL), we have recently studied the behavior of Bi2212 underdoped compound under pressure to resolve the controversy in interpretation of the 600 cm^{-1} band (Blumberg, Kang et al. 1997) (Hewitt, Wang et al. 1999) but the question still remains open (Kendziora, Pelloquin et al. 2000).

PROJECT DESCRIPTION

We propose to tackle with pressure different lattice (phonons), electronic, magnetic, and gap excitations and compare the results with available numerous theoretical predictions. This would lead us to better knowledge of the nature of observed features or even allow studying new phenomena that cannot be perceived without application of pressure.

We will focus on the following topics:

-Extension of the study of the two-magnon feature in the Raman spectra of AF parent materials or underdoped HTSC to ultra-high pressures. One would expect a breakdown of the AF state accompanied by the insulator-metal transition at high pressure. Whether the high-pressure phase is HTSC remains to be seen by other techniques (Struzhkin, Hemley et al. 1997). Also, numerous lower frequency features could be studied in detail to test the proposed hypothesis about their spin-density-wave nature (Zeiger, Strauss et al. 1989).

-Study of the effect of pressure on the phonon modes and electronic background in Hg1201. The electronic structure of this compound with single CuO_2 layer is relatively simple so the complexity of theoretical analysis is greatly reduced. According to calculations (Novikov, Katsnelson et al. 1996), one would expect substantial phonon anomaly under pressure because of pressure induce electronic topological transition. Electronic scattering in this compound is not masked by coupling to phonons (as in YBCO), which makes it an ideal candidate for studying of the gap excitation nature by tuning the doping level by pressure.

Magnetic excitations in transition metal oxides

Transition metal oxides are prototypical examples of strongly correlated electron systems. The strength of electron correlation depends on the ratio between the on-site d-d Coulomb interaction energy U and 3d bandwidth W (Mott 1990). Application of pressure leads to an increase of the 3d bandwidth, so the system can be tuned to induce magnetic, electronic and structural transitions.

Light scattering techniques have been used very extensively for the studying of magnetic excitations in iron-group transition metal compounds (e.g., FeF_2 (Lockwood 1982)). These compounds generally become anti-ferromagnetic at low temperatures, which makes spin-flip (magnons) and electronic (magnetic excitons) transitions collective, thus allowing an appropriate technique for observing them. Raman scattering is a very informative method because the corresponding selection rules strongly favor observation of one- and two-magnon peaks as well as magnetic excitons (Lockwood 1982).

We will extend the Raman and infrared studies of transition metal oxides to ultrahigh pressures. We will concentrate on iron compounds because (i) they show a variety of temperature transitions related to the ordering of spin (charge) subsystems, which can be studied at different pressures, giving a new dimension to those studies (ii) very intriguing transitions related to the suppression of magnetism are expected at ultrahigh pressures.

Magnetite (Fe_3O_4) shows the metal-insulator Verwey transition (ordering of Fe^{2+} and Fe^{3+} irons) at 120 K and ambient pressure (Verwey 1939). The transition is related to an opening of the electronic energy gap and substantial phonon anomalies. A very rich Raman spectrum has been reported in the ordered phase (Gasparov, Tanner et al. 2000), which opens up a possibility for testing these lines for magnetic excitations by applying pressure. Once magnetic excitations are singled out, the Verwey transition will be studied as a function of both pressure and temperature (0-25 GPa, 120-4 K). Combined Raman and IR study will be performed to follow gap (Park, Ishikawa et al. 1998), phonon and magnetic excitation. The results will give new insight into the nature of the Verwey phase and can be compared with the recent high-pressure conductivity (Rozenberg, Hearne et al. 1996) (Morris and Williams 1997) and Mössbauer (Pasternak, Nasu et al. 1996) measurements.

Hematite (Fe_2O_3) is a well-known magnetic material and a wide gap anti-ferromagnetic (T_N=956 K) insulator. Magnetic excitations in this material have been singled out from the numerous phonon bands more than a decade ago (Massey, Bauer et al. 1990). Nevertheless, the Raman spectra of the two-magnon feature at 1525 cm^{-1} have never been traced with pressure. This would give valuable information about antiferromagnetic exchange coupling and its change with interatomic distances. High-pressure transformation at 50 GPa will also be examined to test its insulator-metal magnetic-nonmagnetic nature (Pasternak, Rozenberg et al. 1999) (Badro, Fiquet et al. 2002).

Wüstite (FeO) is a paramagnetic insulator at ambient conditions and it transforms to an anti-ferromagnetic state at a temperature below 190-210 K. Our preliminary measurements reveal a presence of Raman magnetic excitation below T_N, which can be used to determine the exchange interactions and spin-orbit coupling. Thus, the magnetic state could be probed to high pressures, which can be used to test current ideas about the nature of the high-pressure phase (Pasternak, Taylor et al. 1997) (Badro, Struzhkin et al. 1999).

A possible magnetic collapse (or high-spin low-spin transition) in transition metal monoxides has been predicted by first-principle calculations (Isaak, Cohen et al. 1993) (Cohen, Mazin et al. 1997) at pressures within the reach of current diamond anvil cell techniques. According to calculations, the first candidate for the magnetic collapse transition is CoO (90 GPa). A group including PI has studied magnetic excitations in CoO under moderate pressure (17 GPa) some time ago (Struzhkin, Goncharov et al. 1993). We will extend these measurements to megabar pressure range. A preliminary x-ray diffraction study performed in our group showed structural changes in CoO at 80 GPa (Guo, Mao et al. 2000), which could be related to the expected transition.

A collapse of magnetic moments resulting from insulator-metal or high-spin low-spin transition has also been detected in other transition metal compounds by Mössbauer spectroscopy (Pasternak, Taylor et al. 1997; Pasternak, Rozenberg et al. 1999), electrical conductivity (Pasternak, Rozenberg et al. 1999) and x-ray emission spectroscopy (Badro, Struzhkin et al. 1999) (Badro, Fiquet et al. 2002). These results are often controversial, which stimulates optical studies with the whole range of techniques available. This mainly includes Raman measurements, but concurrent study of optical properties in IR, visible and UV range will be also performed to study possible IR active magnetic excitation (see Ref. (Struzhkin, Goncharov et al. 2000)), the charge transfer gap and free-electron response (in case of insulator-metal transition).

D. Optical techniques – current status and future development

Infrared synchrotron spectroscopy

Infrared synchrotron spectroscopy is a fast developing technique, which utilizes the advantage of a 10^4 times brighter light source as opposed to a conventional one for making more rapid measurements with higher spatial resolution (Frahm, Ando et al. 1995). High-pressure IR synchrotron spectroscopy was pioneered by the Geophysical Laboratory in 1991, which lead to breakthrough results like the discovery of a large infrared activity in solid hydrogen (Hanfland, Hemley et al. 1993) and demonstration of symmetric hydrogen bond formation in compressed ice (Goncharov, Struzhkin et al. 1996).

The NSLS presented us with an opportunity to construct a fully dedicated high-pressure synchrotron beam line at the rebuilt U2 port, which has a much larger aperture and hence gives significantly higher intensity in IR, particularly at long wavelengths. The installation of the beam line is now complete, and the beam line is open for the general user.

IR synchrotron spectroscopy technique has been developed significantly in the past years. Far-IR measurements in megabar pressure range have been performed (Goncharov, Struzhkin et al. 1999). Mid-IR measurements have been extended to 285 GPa pressure range. First preliminary data on far-IR reflectivity at low temperatures has been obtained. High-quality far-IR measurements of olivine and other minerals under moderate pressure (to 10 GPa) have been extended to a 50 cm^{-1} spectral range.

Raman technique at high pressures

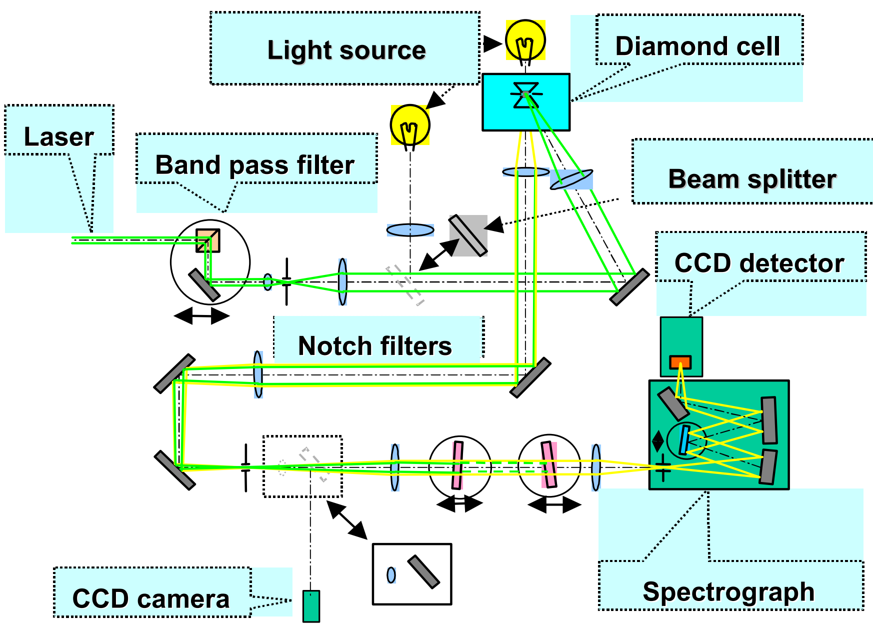

Fig. 1. Optical layout of the Raman system capable of performing ultrahigh pressures measurements in opaque (e.g., metal) samples.

Raman technique has experienced substantial development in the last decade. This is related to the development of sensitive two-dimensional charge-coupled-devices (CCD) detectors and holographic optics (e.g., notch filters). We developed a new type of Raman apparatus, which uses extensively holographic transmission optics. Holographic transmission gratings (HTG) have a much larger throughput compared to commonly used surface relieve ones. Moreover, they allow the design of much more compact and flexible spectral devices than conventional ones. These properties of HTG have been known for quite a while, yet the development of versatile and convenient for scientific use instruments has been retarded by the difficulty of changing of the spectral range in the case of HTG. Using of snap-in grating or stack of gratings is quite adequate for industrial application, but cannot be satisfactory for scientific application, when fast and easy change of the spectral range and excitation frequency is necessary.

We developed a unique design (Goncharov and Struzhkin 2000) of universal filter stage with HTG as a dispersive element, which can be tuned over a large spectral range without realignment. This stage can be used as a bandpass filter, dispersive laser beamsplitter, laser rejection filter, and spectrograph. We have routinely used in our lab the bandpass filter of the described design for past a couple of years, achieving superior results. Other applications have been tested and are at the stage of design and assemblage. Use of HTG for the laser rejection filter has proven as extremely promising for measurements of low-frequency (to 10 cm^{-1}) Raman spectra, those being normally unattainable if using notch rejection filters. Triple grating spectrometers (e.g., JobinYvon XY) routinely used for this purpose are too bulky and have substantially lower throughput compared to the newly designed. Moreover, the HTG based devices show better stray light rejection in the vicinity of the excitation wavelength. This is vital for the research proposed since the low-frequency (10-100 cm^{-1}) Raman response contains very important information (e.g., electronic scattering). We are requesting funding for building a double monochomator-filter based on HTG elements.

Raman/fluorescence systems (Fig. 1) in our Washington DC located group and at the NSLS are used routinely for ruby fluorescence measurements, ultra-high pressure Raman measurements at ambient conditions, ultra-high pressure Raman measurements at low (L-He) temperatures, and high temperatures (to 500 K; to 1000K is under construction). The excitation wavelength can be varied from 457 nm (Ar ion laser) to 950 nm (Ti-sapphire laser). This facility has proven to be extremely efficient and is operating in multi-user arrangement. Moreover, many scientist who work outside of the lab use the facility. Some of them are I-Ming Chou and Robert C. Burruss, U.S. Geological Survey; Sean Shieh, Princeton University; Dmitri Reznik, NIST; David McKeown, Catholic University; Chris Kendziora, NRL; Sebastian Merkel, EN Lyon; Somayazulu Maddury, HP CAT; Achintya Maddury, Thomas Jefferson high school; James Badro, University of Paris; Eran Karmon, UC Berkeley; Eugene Huang, Institute for Earth Science, Taiwan. We are requesting funds for further improvement and upgrading of the facility, so it could better suit numerous users. This includes research and development work for improving the optical hardware and combining it with the optical cryostat. If this project is funded, it will give many more external users a chance to get trained and to use our facility for scientific studies.

Raman spectroscopy is going to be one of the major experimental techniques of the project proposed. We propose Raman studies under pressure of the samples with extremely low signal levels like metals and HTSC. These measurements can only be feasible if the spurious background scattering is negligible. The main background source for the high-pressure studies is diamond fluorescence. Only the highest quality diamonds with fluorescence level less than 10^{-3} (compared to the intensity of the first order Raman peak of diamond) suits these measurements. In addition, many low-fluorescence natural diamonds increase fluorescence significantly at low temperatures and/or high pressures. Artificial ultrapure diamonds (Vohra and Vagarali 1992) have proven to be ideal in this case. Our strategy would be to use those kinds of diamonds in case breakthrough results are expected. We have proved this strategy in our previous studies (see e.g. (Merkel, Goncharov et al. 2000)). We are requesting the funding for purchasing of artificial ultrapure diamonds from the Sumitomo Corporation in Japan.

PROJECT DESCRIPTION

Visible and UV reflectivity and transmission

During the past several years, there has been a tremendous need for an IR-visible-VUV reflectivity and transmission system capable of operating at ultra-high pressures (see, e.g. (Syassen and Sonnenschein 1982). For the routine mid- and near-IR measurements we use Nicolet 750 Magna FT-IR spectrometer coupled to a custom made infrared microscope. The same bench can be also used for IR low-temperature transmission measurements. Visible transmission spectra have been measured with the Raman setup by measuring spectra in a number of spectral windows and then "gluing" them. The goal of this project requires building of a dedicated and integrated facility for studying of optical properties in a wide spectral range. We already possess all major parts of the system- FT-IR spectrometer, UV-visible grating monochromator-spectrograph with CCD detector, UV-visible light source, and a custom made Cassegrain-type mirror optics. We are requesting the funding for the completion of this work, which includes some mirror optics and holders.

E. Milestones for the proposed research

Year 1

- Development of low-frequency holographic rejection filter for high-pressure Raman measurements
- Raman and IR studies of phonon, electron, and magnetic excitations in Fe_3O_4, Fe_2O_3, FeO close to spin crossover (collapse) and insulator-metal transition
- Study of the effect of pressure on the phonon modes and electronic background in Hg1201 with different doping levels
- High-pressure polarization studies of electronic background features in V_2O_3, FeSi close to the insulator-metal transition

Year 2

- Completion of the dedicated V-UV absorbance/reflectivity facility.
- Raman, IR, V-UV studies of CoO, MnO, NiO to very high pressures, approaching spin crossover and insulator-metal transition
- Extension of the study of the two-magnon feature in the Raman spectra of AF parent material (e.g., La_2CuO_4, or underdoped HTSC) to ultra-high pressures. One would expect breakdown of AF state and insulator-metal transition. Also, numerous lower frequency features could be studied in detail to test the proposed hypothesis about their spin-density-wave nature (Zeiger, Strauss et al. 1989).

F. Feasibility and anticipated results

To accomplish the goals of the project, we will be primarily using optical methods, while other available techniques for the same materials or even samples will be complementary and supported by other funding sources. These techniques include x-ray diffraction to determine structural parameters, magnetic susceptibility and electrical resistivity measurements for obtaining information about static conductivity, superconductivity and magnetic properties, x-ray spectroscopic techniques to probe dynamical structure factor and electronic structure. Our laboratory and beam lines to which we have access contain all the necessary instrumentation for the proposed experiments, including diamond anvil cells, He cryostats, x-ray instrumentation, and magnetic susceptibility and electrical conductivity instrumentation (see Facilities, equipment and other resources section for more detail).

As mentioned above, several feasibility measurements have been already done. This includes measurements of Raman in Fe: Ni alloy (with Eugene Huang, Institute for Earth Science, Taiwan), Raman in FeO, CoO and Fe at low temperature, Raman in Re, Co to megabar pressures, Raman studies in Fe_3O_4 at low temperatures to 20 GPa (with L. Gasparov). We are in the process of designing and testing new ideas for a modified Raman setup, which includes the possibility of measuring low-frequency Raman (to 10 cm^{-1}) at ultrahigh pressures. Funding is required to complete these preliminary works and developments (see Facilities, equipment and other resources section).

The project will give new insights into the origin of the electronic and magnetic excitations in d-metal-based compounds, superconductors and insulators by systematic studies of their properties through changing their volume. We also expect qualitatively new results related to the application of ultra-high pressures (high-T_c superconductors, simple oxides of d-metals) . This will lead to a more extended knowledge and possibly new phenomena in metals, superconductors and insulators, to a broader impact on education of qualified researchers, but none of this can be successfully completed without the funding requested for the present proposal.

This work in LLNL will be performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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PROJECT DESCRIPTION